

Translation of Japanese Patent No. 2639463 filed by Tonen Corp.

[Title of the Invention] Process for preparing 1,4-butanediol and tetrahydrofuran 4

[What is Claimed is]

[Claim 1] A process for preparing 1,4-butanediol and tetrahydrofuran by subjecting maleic anhydride and/or succinic anhydride to a catalytic hydrogenation in a gas phase in the presence of a solid catalyst containing copper, zinc and aluminum.

[Detailed Explanation of the Invention]

Industrial Field for Utilization

The present invention relates to a process for preparing 1,4-butanediol and tetrahydrofuran, more specifically to a process for preparing 1,4-butanediol and tetrahydrofuran by subjecting maleic anhydride and/or succinic anhydride to a catalytic hydrogenation in a gas phase in the presence of a solid catalyst containing copper, zinc and aluminum.

Prior Art

1,4-butandiol is a useful compound as a raw material for preparing a polybutyleneterephthalate resin and a polyurethane resin. Therefore, it is strongly desired to develop a production method of 1,4-butanediol that can be conducted cheaply and efficiently.

Conventionally known methods for preparing γ -butyrolactone or 1,4-butanediol by means of catalytic hydrogenation of maleic anhydride and/or succinic anhydride or the derivatives of these are disclosed as the followings:

- (a) Preparation of α -butyrolactone by the catalytic hydrogenation of maleic anhydride or succinic anhydride in a gas phase by use of a catalyst comprising zinc-copper-chromium (JP-B 44 (1969)-32567).
- (b) Preparation of γ -butyrolactone by the catalytic hydrogenation of maleic anhydride and/or succinic anhydride in a gas phase in the presence of a reduction catalyst of copper oxide - beryllium oxide - zinc oxide (JP-B 47 (1973)-28294).
- (c) Preparation of 1,4-butanediol by the hydrogenation of maleic anhydride and/or succinic anhydride in a liquid phase under the presence of a catalyst comprising elements of subgroup VII and subgroup VIII or compounds thereof (JP-A 51 (1976)-133212).
- (d) Preparation of 1,4-butanediol by the hydrogenolysis of maleic diester and

fumaric diester in a gas phase under the presence of copper chromite catalyst (JP-A 61 (1986)-22035 and JP-A 62 (1987)-501702).

Moreover, the inventors of the present invention proposed a process for preparing 1,4-butanediol by the catalytic hydrogenation of maleic anhydride and/or succinic anhydride in a gas phase under the presence of a catalyst of copper oxide - zinc oxide (JP-A 63 (1988)-175062).

On the other hand, tetrahydrofuran is a useful compound as a raw material for polytetramethylene glycol or the like and a solvent for polyvinyl chloride or polyurethane, of which production method, in addition to the production of 1,4-butanediol, is desired to be developed to give the material cheaply and efficiently.

Conventionally known methods for preparing tetrahydrofuran by means of catalytic hydrogenation of maleic anhydride and/or succinic anhydride are disclosed as the followings:

- (a) Preparation of tetrahydrofuran with the hydrogenation and dehydration of maleic anhydride and/or succinic anhydride and/or γ -butyrolactone, etc in a gas phase under the presence of a mixed catalyst of copper-based catalyst and dehydration catalyst (JP-B 48 (1972)-30272).
- (b) Preparation of γ -butyrolactone and/or tetrahydrofuran by the hydrogenation of maleic anhydride and/or succinic anhydride, etc in a liquid phase under the presence of a solid catalyst comprising palladium, cobalt and niobium (JP-A 62 (1987)-111975).

Furthermore, the inventors of the present invention proposed a process for preparing tetrahydrofuran and 1,4-butanediol by conducting hydrogenation of maleic anhydride and/or succinic anhydride in a gas phase under the presence of a solid catalyst comprising copper, chromium and manganese (JP-A 63 (1988)-313760).

Object to be Solved by the Invention

The above-mentioned method for preparing 1,4-butanediol, however, has problems as follows. Namely, the above-mentioned methods for performing hydrogenation of maleic anhydride and/or succinic anhydride in a gas phase in the presence of a catalyst, except the method proposed by the inventors of the present invention give only γ -butyrolactone, and the aimed 1,4-butanediol cannot be obtained. Moreover, in the methods wherein the hydrogenation of maleic anhydride and/or succinic anhydride is performed in a liquid phase under the presence of a catalyst, it is necessary to apply a high pressure of about 200 kg/cm².

Accordingly, problems are accompanied with these methods as that huge installation cost and operation cost are required. The method of performing hydrogenolysis of maleic diester or the like in a gas phase in the presence of a catalyst does not require such a high pressure as mentioned above, but the method has the problem that the production steps is extremely complicated since a diesterification step is necessary. In other words, the reaction to convert monoester to diester is an equilibrium reaction, so that two reaction steps are necessary to fully progress the reaction. In this reaction, it is necessary to add 3 reaction steps with the monoesterification step taken into consideration.

On the other hand, the processes for preparing tetrahydrofuran, as described above, have the problems as follows. In the process for preparing tetrahydrofuran from maleic anhydride or the like in the presence of a mixed catalyst of a copper-based catalyst and a dehydrogenation catalyst, there are such problems that a reaction unit is complicated and the production steps comes to be complicated since it is necessary in this method to perform hydrogenation and dehydrogenation in three divided reaction zones. In the case of the process wherein a catalyst comprising palladium, cobalt and niobium is employed, there are problems of high pressures being required for performing hydrogenation reaction in a liquid phase, and of giving γ -butyrolactone as a by-product in a large quantity.

Moreover, there was not conventionally known the simultaneous production method of 1,4-butanediol and tetrahydrofuran by the catalytic hydrogenation of maleic anhydride and/or succinic anhydride in a gas phase, except the method proposed by the inventors of the present invention.

It is the object of the present invention to provide a method for simultaneously producing 1,4-butanediol and tetrahydrofuran cheaply and efficiently with eliminating the problems in the prior arts as that the installation cost and operation costs are expensive and the production steps are complicated in the course of producing 1,4-butanediol and tetrahydrofuran from maleic anhydride and/or succinic anhydride.

Means to Solves the Problems

Summary of the Invention

The inventors of the present invention thought that it is possible to have a large merit if 1,4-butanediol and tetrahydrofuran could be produced by a direct hydrogenation of maleic anhydride and/or succinic anhydride under a low pressure, and they variously studied such hydrogenation method in a gas phase.

Moreover, they thought the reason why only γ -butyrolactone had been obtained in the gas phase hydrogenation of maleic anhydride and/or succinic anhydride was that all the methods employ a low hydrogen/raw material ratio and the reactions were performed with pressures around the atmospheric pressure. The inventors of the present invention have found that it is possible to simultaneously produce 1,4-butanediol and tetrahydrofuran in a high yield by the hydrogenation reaction with a higher hydrogen/raw material ratio than the conventional ones, under a pressure condition within a range wherein the gas phase can be kept. Thus, the present invention has been completed.

Namely, the present invention relates to a process for preparing 1,4-butanediol and tetrahydrofuran by the direct hydrogenation of maleic anhydride and/or succinic anhydride, characterized in that a reaction in a gas phase is performed under the presence of a solid catalyst comprising copper, zinc and aluminum.

Catalyst

The catalyst for use in the present invention is the one obtained by reducing copper oxide · zinc oxide · aluminum oxide catalyst beforehand. This sort of catalyst is prepared, for instance, by dissolving a copper compound such as copper nitrate, zinc compound such as zinc nitrate and aluminum compound such as aluminum nitrate, adding aqueous sodium carbonate dropwise thereto with stirring under the heat application until the solution becomes neutral to mix the same, recovering a solid thus obtained by filtration, drying and calcinating the material, followed by forming to have a predetermined shape with the use of a molding equipment. In this preparation method, a copper oxide · zinc oxide · aluminum oxide catalyst is obtained.

The reduction of the catalyst for use in the present invention is performed by the treatment of applying nitrogen gas containing 2 vol.% of hydrogen to the catalyst over a whole day and night, at 170 °C under the pressure of several tens kg/cm²G, with a gas hourly space velocity (G.H.S.V.) with the convention to an ordinary temperature/ordinary pressure basis (hereinafter G.H.S.V. is always referred to as converted values to an ordinary temperature/ordinary pressure basis) of about 2400 hour⁻¹, and further applying the gas with a catalyst bed temperature being set at 200 °C for several hours and with a hydrogen concentration being set as 100 vol.% by the gradual increase of the concentration.

Solvent

The solvents for use in the present invention are not particularly limited.

The examples thereof are γ -butyrolactone, tetrahydrofuran, dimethyl ether, diethyl ether, 1,4-dioxane. Among these, γ -butyrolactone is particularly preferable because it is a good solvent for maleic anhydride and succinic anhydride; it is one of the products obtained by the hydrogenation; and it is considered to be an intermediate of 1,4-butanediol. It is also possible not to use a solvent.

Catalytic Condition

The contact of the gas mixture containing maleic anhydride and/or succinic anhydride and hydrogen gas with the catalyst is performed by appropriately selecting a method from conventionally known methods. For example, it is possible to use a method of contacting the gas mixture with the catalyst in the fixed bed, a method of contact by use of a moving bed, or a method of contact of using a fluid bed. Depending upon cases, it is also possible to batchwise contact the gas mixture with the catalyst.

The contact time of the gas mixture containing maleic anhydride and/or succinic anhydride and hydrogen gas with the catalyst is 1000 to 100000 hours⁻¹, preferably about 1500 to 20000 hour⁻¹ as G.H.S.V.

The reaction temperature for use in the present invention is about 170 to 280 °C, and the molar ratio of hydrogen gas to maleic anhydride and/or succinic anhydride is about 50 to 1500. The reaction temperature, reaction pressure and hydrogen gas/raw material ratio to be employed are appropriately selected from ranges where the system can be kept in a gas phase.

Here, when the molar ratio of hydrogen gas/raw material is less than 50, it tends to cause the decrease of the reaction ratio and to cause the deterioration of the catalyst due to the formation of carbon-like products, while when the molar ratio exceeds 1500, a large amount of hydrogen must be recycled, that is economically disadvantageous, so that neither cases are preferable.

The formation ratio of 1,4-butanediol and tetrahydrofuran in the products of the present invention differs depending on the ratio of composition, reaction pressure and reaction temperature. In general, however, the molar ratio of tetrahydrofuran/1,4-butanediol is set in the range of 1/50 to 100/0.

Moreover, 1,4-butanediol and tetrahydrofuran in the reaction mixture after the completion of the reaction can be easily separated by use of a known method such as distillation.

Effect of the Invention

According to the process of the present invention, it is possible to obtain

1,4-butanediol and tetrahydrofuran from maleic anhydride and/or succinic anhydride in a single step reaction at a high yield with a remarkable simplification of the production process. Furthermore, it is possible to attain effects of reducing an installation cost and operation cost since 1,4-butanediol and tetrahydrofuran can be prepared in the present invention, under a far low pressure in comparison with the hydrogenation technology in a liquid phase.

The present invention will now be explained with referring to Examples, to which the present invention is not restricted.

Example 1

A reaction vessel for a fixed bed (15 mm ϕ \times 600 mm) was filled with 15cc of a commercially available copper-aluminum-based oxide catalyst (made by Toyo CCI K.K.; product name: C18-1) containing copper, zinc and aluminum as metals respectively in amounts of 16.0 wt.%, 35.0 wt.% and 9.6 wt.%, to which pressure application was made to 40 kg/cm²G in the stream of nitrogen with the application of heat to 170 °C. Thereafter, hydrogen was gradually added to the nitrogen gas stream, and the nitrogen gas containing 2 vol.% of hydrogen was introduced overnight at 40 kg/cm²G, 170 °C, G.H.S.V. of 2400 hour⁻¹. Further, the hydrogen concentration was gradually increased to 100 vol.% with carefully watching that the catalyst bed temperature does not exceed 200 °C, and reduction treatment was performed at 40 kg/cm²G, 200 °C, G.H.S.V. of 2400 hour⁻¹ for two hours.

With the heat application to the above-mentioned fixed-bed reaction vessel to 230 °C, a solution of maleic anhydride in γ -butyrolactone (molar ratio of maleic anhydride/ γ -butyrolactone=1/1) and hydrogen were fed against maleic anhydride and γ -butyrolactone at a ratio of 200 moles (former) to 1 mole in total (latter) under the condition of pressure of 40 kg/cm²G and of G.H.S.V. of 9600 hour⁻¹. The product was analyzed by mean of gas chromatography, and the identification of the product was carried out by GC-MS. As a result, it was found that maleic anhydride had a conversion ratio of 100 mol%, and that 22.2 mol% of 1,4-butanediol, 72.2 mol% of tetrahydrofuran and 4.2 mol% of n-butanol were formed based on maleic anhydride employed. In the products, succinic anhydride was not detected.

Example 2

The reduction treatment of the catalyst and the reaction were performed in the same way as in Example 1 except that the pressure in the course of the reduction treatment of the catalyst and the reaction pressure were set as 15 kg/cm²G, reaction temperature was changed to 210 °C, and the molar ratio of

maleic anhydride and γ -butyrolactone was changed to 1/3, and the G.H.S.V was set as 3200 hour⁻¹.

As a result, it was found that maleic anhydride had a conversion ratio of 100 mol%, and that 12.9 mol% of 1,4-butanediol, 80.5 mol% of tetrahydrofuran and 3.2 mol% of n-butanol were formed based on maleic anhydride employed. In the products, succinic anhydride was not detected.

Example 3

The reduction treatment of the catalyst and the reaction were performed in the same way as in Example 2 except that a commercially available copper-zinc-aluminum-based oxide catalyst containing as metals, copper, zinc and aluminum respectively of 26.0 wt.%, 30.6 wt.% and 5.0 wt.% (made by Toyo CCI K.K., product name: C18-HC).

As a result, it was found that maleic anhydride had a conversion ratio of 100 mol%, and that 29.9 mol% of 1,4-butanediol, 65.5 mol% of tetrahydrofuran and 4.6 mol% of n-butanol were formed based on maleic anhydride employed. In the products, succinic anhydride was not detected.

Example 4

The reduction treatment of the catalyst and the reaction were performed in the same way as in Example 2 except that a commercially available copper-zinc-aluminum-based oxide catalyst containing as metals, copper, zinc and aluminum respectively of 19.3 wt.%, 29.2 wt.% and 9.1 wt.% (made by Toyo CCI K.K., product name: MDC2).

As a result, it was found that maleic anhydride had a conversion ratio of 100 mol%, and that 40.0 mol% of 1,4-butanediol, 28.0 mol% of tetrahydrofuran and 1.3 mol% of n-butanol were formed based on maleic anhydride employed. In the products, succinic anhydride was not detected.

Example 5

The reduction treatment of the catalyst and the reaction were performed in the same way as in Example 2 except that a commercially available copper-zinc-aluminum-based oxide catalyst containing as metals, copper, zinc, aluminum and calcium respectively of 21.1 wt.%, 42.5 wt.%, 4.0 wt.% and 1.0 wt.% (made by Toyo CCI K.K., product name: C61).

As a result, it was found that maleic anhydride had a conversion ratio of 100 mol%, and that 8.4 mol% of 1,4-butanediol, 44.0 mol% of tetrahydrofuran and 2.6 mol% of n-butanol were formed based on maleic anhydride employed. In the products, succinic anhydride was not detected.

for copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), 119.0 g of zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and 75.03 g of aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were dissolved in 600 ml of water. Aqueous sodium carbonate of which concentration is one mol/L was dropwise added to the above solution with the temperature of the latter being maintained at 70 to 75 °C with stirring until pH of the solution reached 7.3, and thereafter, the stirring was continued with the solution kept at about 80 °C for 90 minutes. The solution was allowed to cool, then a solid obtained was separated by filtration, which was washed with passing 10 L of warm water at 60 °C therethrough. Subsequently, the solid was dried at 120 °C for 12 hours under the stream of air, and then subjected to calcination at 400 °C for 3 hours, whereby a solid in an amount of 6 g was obtained. The solid thus obtained was formed and ground, followed by being sieved to obtain 6 to 10 mesh fraction, so that a solid catalyst based on copper oxide, zinc oxide and aluminum oxide was obtained. The catalyst thus obtained had contents of copper, zinc, and aluminum as metals respectively of 18.3 wt.%, 36.0 wt.% and 8.6 wt.%.

The reduction treatment of the catalyst and the reaction were performed in the same way as in Example 2 with the use of 15 cc of the catalyst prepared above.

As a result, it was found that maleic anhydride had a conversion ratio of 100 mol%, and that 5.6 mol% of 1,4-butanediol, 57.2 mol% of tetrahydrofuran and an extremely minute amount of n-butanol were formed based on maleic anhydride employed. In the products, succinic anhydride was not detected.

Example 7

The reduction treatment of the catalyst and the reaction were performed in the same way as in Example 2 except that maleic anhydride employed was changed into succinic anhydride. Thus, reaction products with the almost same composition as that in Example 2 were obtained.

Example 8

A solution of maleic anhydride in 1,4-dioxane (molar ratio of maleic anhydride/1,4-dioxane=1/3) and hydrogen were fed against maleic anhydride in the ratio of 800 moles (former) to 1 mole (latter) at 210 °C under the pressure of 15 kg/cm²G, at G.H.S.V. of 3500 hour⁻¹.

As a result, it was found that maleic anhydride had a conversion ratio of 100 mol%, and that 94.1 mol% of tetrahydrofuran and 4.9 mol% of n-butanol were formed based on maleic anhydride employed. In the products, succinic anhydride,